High-Resolution Carbon 1s Photoelectron Spectrum of Small Molecules

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A challenge for inner-shell photoelectron spectroscopy has been the study of organic molecules in which the carbon atoms have similar ionization energies even though they are quite distinct chemically. A typical example is propene, $CH_3CH=CH_2$, whose three carbons have very different chemical reactivity, but core-ionization energies that differ by only 0.56 eV [1]. Only recently has it been possible to resolve the contributions from these carbons in the carbon 1s photoelectron spectrum of this molecule and to correlate the ionization energies with the reactivity.[1] The very high resolution capabilities of the Advanced Light Source present a long-awaited opportunity to examine inner-shell photoelectron spectra of such molecules and to gain chemical insights that were previously inaccessible.

The complete analysis of such a spectrum requires an understanding of a number of factors: the vibrational excitation that occurs during ionization, the line broadening that results from the finite lifetime of the core-ionized state, and the distortion of the line shape that results from interaction of the outgoing photoelectron with the Auger electron (emitted in the deexcitation of the core hole). In addition it is necessary to understand the instrumental features that affect the spectrum. These include the calibration of the energy scales of the monochromator and electron-energy analyzer, the resolution of the photon beam, the resolution of the electron-energy analyzer, and the variation of the analyzer transmission with electron energy.

Our program during 1997 aimed at providing the basis for this understanding with measurements of a number of simple carbon containing molecules: CH_4, CO, CO_2, CF_4, and $H_2C=CH_2$. In addition it included studies of the carbon 1s photoelectron spectra of several novel molecules for which lower resolution studies showed that we would benefit from the high-resolution available at the Advanced Light Source. These included $SF_5CH_2CH_3$, SF_5CHCH_2, and SF_5CCH, molecules, which illustrate the interaction of the highly electronegative SF_5 group with singly, doubly, and triply bonded systems.

For most of these measurements, the analysis is still in progress. However, the work on ethene ($H_2C=CH_2$) has been published and illustrates many of the features of these spectra. [2]

The carbon 1s photoelectron spectrum of ethene

When core-ionization takes place in a molecule, there is typically vibrational excitation of the resulting ion, leading to vibrational structure in the photoelectron spectrum. This structure can be regarded as an opportunity for elucidating the changes in bond lengths and angles that accompany photoionization, or it can be regarded as a challenge to be dealt with in achieving understanding of other features of the spectrum, such as the resolution of contributions from inequivalent carbon atoms with similar ionization energies. In understanding this vibrational structure it is helpful to have guidance from ab initio theory.

In other studies [3] we have shown that a relatively simple level of ab initio theory gives reasonably accurate predictions of the carbon 1s photoelectron spectra of a number of simple hydrocarbons. The measurements on ethene provided us with an opportunity to test this approach with data collected at higher resolution than had been possible previously. The ethene spectrum collected on beam line 9.0.1, with an experimental resolution of 55 meV is shown in Fig. 1 as the points. Here it is compared with our theoretical predictions of the spectrum, shown as the solid line. The shape of the curve has been predicted entirely from ab initio theory, and the only adjustable parameters are the overall height and position and a constant background. The theory is relatively simple and, considering its simplicity, the agreement between experiment and theory is quite satisfactory.

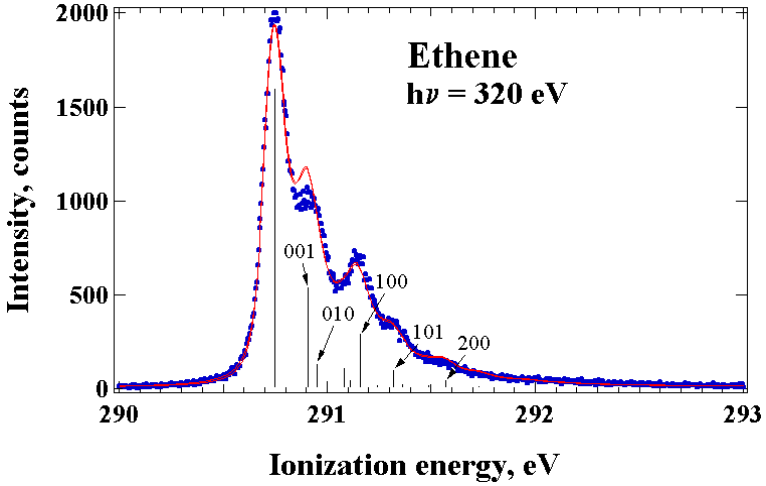

Figure 1. Experimental and calculated photoelectron spectra for carbon 1s photoionization in ethene. The points show the experimental data. The vertical lines show the positions and intensities of 14 of the predicted vibrational transitions. Several of these are labeled with the appropriate vibrational quantum numbers. The solid line represents the predicted vibrational structure dispersed so as to show the combined effects of experimental resolution, lifetime, and post-collision interaction. The overall intensity and position of this line as well as a constant background have been fit to the experimental data by least squares.

REFERENCES

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